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(56) Documents Cited

**GB 1525236 A** **WO 2001/070646 A1**  
**US 4933031 A** **US 4642137 A**  
**US 3486917 A**

**WPI Abstract Accession No.2000-467906 &**  
**JP2000319052**

**WPI Abstract Accession No.1996-514784 & JP8268736**

(58) Field of Search

**UK CL (Edition T ) C1H**

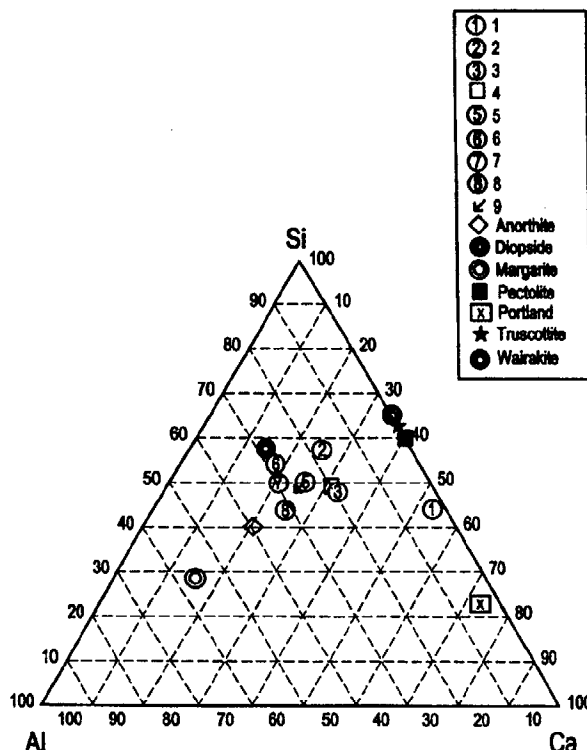
**INT CL<sup>7</sup> C04B**

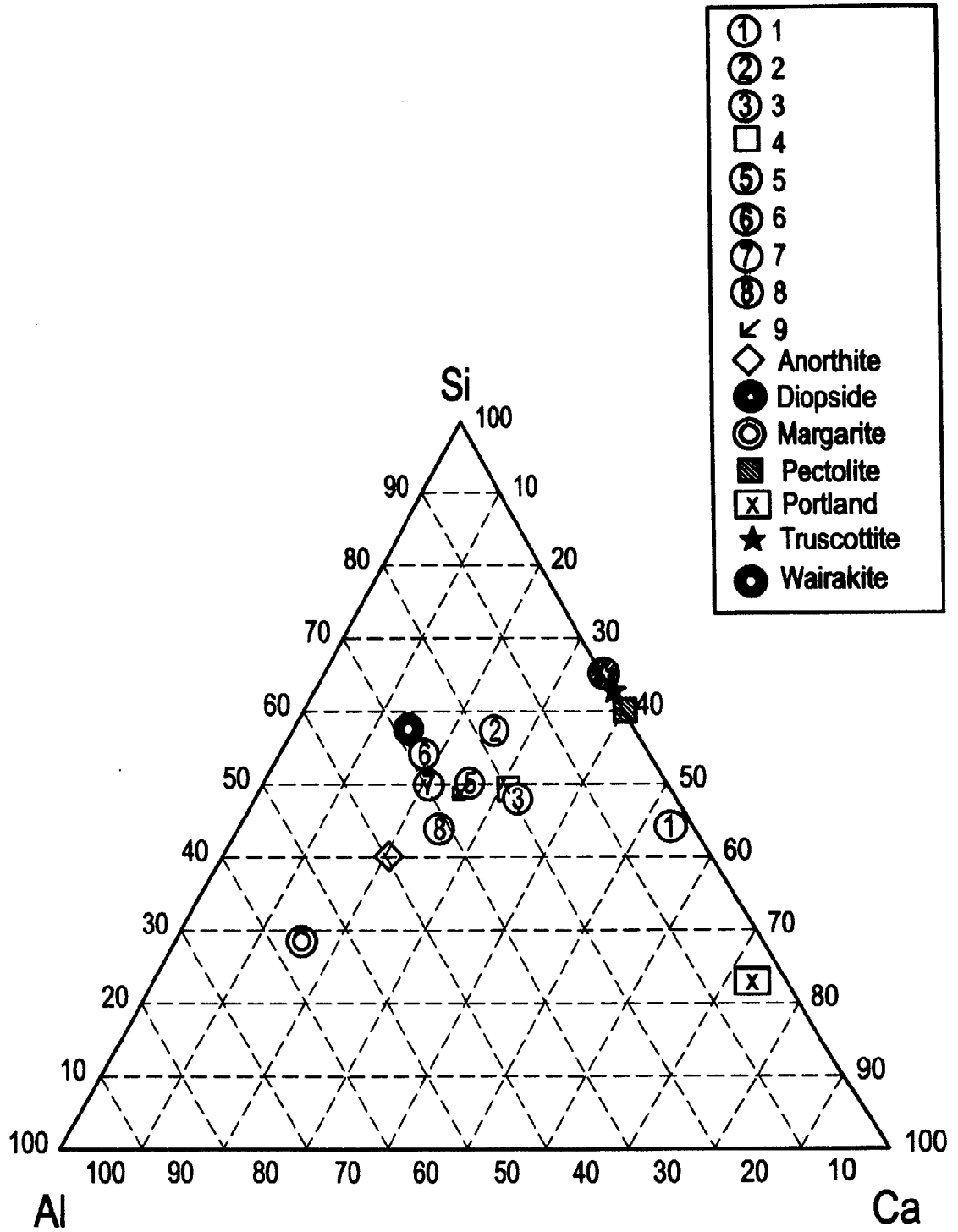
**Other: Online: WPI, EPODOC, PAJ**

(54) Abstract Title

**Cement composition that promotes the formation of anorthite**

(57) A cement composition comprising a mixture of: (i) an hydraulic cement; and (ii) one or more additives that contribute Si, Ca or Al to the mixture; has a mineralogical composition within the margarite-quartz-pectolite region of the Si-Ca-Al phase diagram. The constituents are selected to optimise the formation of anorthite when the cement is used in high temperature oil, gas, water or geothermal wells. Anorthite provides a strong and durable matrix at these temperatures (250 to 400°C). For 100 parts of cement, the additives may include 11.5-80 parts silica, 28-143 parts kaolin / metakaolin and 14.8-72 parts fly ash. Preferably the average particles size of the kaolin / metakaolin is 2 to 10µm, of silica is 2 to 330µm, and of fly ash is 50-400µm.





## CEMENTING COMPOSITIONS AND METHODS FOR HIGH TEMPERATURE WELLS.

The present invention relates to cement compositions and placement techniques suitable for the construction of wells, for example oil, gas, water or geothermal wells or the like. The invention relates in particular to cementing compositions suitable for high temperature wells.

After drilling an oil well or the like, a casing is often lowered into the hole and the annulus between the outside of the casing and the borehole wall is filled with cement over all or part of its extent. This cementing prevents exchange of fluids between the different layers of formation traversed by the hole, prevents gas from rising in the annular space surrounding the casing or limits the ingress of water into the production well. The cement also supports the casing and the borehole.

In most cases, a Portland cement is used as a hydraulic binder, a material which is essentially a mixture of calcium silicates and calcium aluminosilicates. In the presence of water, the various mineral phases hydrate and form, inter alia, hydrated calcium silicate (CSH) and also portlandite ( $\text{Ca(OH)}_2$ ) and aluminium sulphate. CSH is a gel which is largely responsible for the cohesion and mechanical strength of the cement in the short to medium term.

When the temperature exceeds about  $100^\circ\text{C}$ , in the first days or months the majority of cements lose compressive strength and become permeable.

This phenomenon, known as retrogression, is due to metamorphosis of CSH gel to a highly crystalline phase known as alpha dicalcium silicate,  $\alpha\text{-C}_2\text{SH}$ , which is much denser than CSH with a contraction in volume and an increase in the porosity of the cement. This results in disintegration of the cement which increases in rate as the porosity increases, rendering it more sensitive to chemical attack due for instance to inflow of brine or carbon dioxide from the reservoir.

To avoid the phenomenon of retrogression, silica in the form of sand or silica flour is systematically added to compositions which have to withstand temperatures of more than  $100^\circ\text{C}$ . Adding 35% to 40% of silica (with respect to the mass of the Portland cement "BMO") brings the  $\text{CaO/SiO}_2$  ratio (usually denoted C/S) to about unity.

Under such conditions, CSH then transforms at about  $110^\circ\text{C}$  to tobermorite  $\text{C}_5\text{S}_6\text{H}_5$  then to xonotlite  $\text{C}_6\text{S}_6\text{H}$  if the temperature is raised to  $150^\circ\text{C}$ . Those phases ensure the stability of the cement at high temperature, in the absence of brine. Those two minerals are intrinsically very strong but they have slightly different apparent densities, which destabilises the cement.

The degradation mechanisms described above are certainly not exhaustive, not least because the roles of other oxides present in the Portland cement, in particular alumina and ferrites, have been ignored, but they suffice to demonstrate the complexity of the phenomena occurring, without even considering the reaction products between the cement matrix and brines. In nature, in a geological medium, cement is thus metastable. In contact with brine or carbon dioxide, its mineralogical repertoire is modified by ion exchanges, which modify its physical qualities.

The problems of cement disintegration when the temperature is raised are more severe when developing very deep wells, or injecting steam to recover highly viscous oils, or in geothermal wells to exploit geothermal energy.

French patent FR-A-2 765 571 proposes selecting a mineralogical phase which is stable at the envisaged temperatures and pressures and promoting its formation by adding a certain quantity of a mineral oxide to a base constituted by Portland cement and silica. In particular, it describes compositions which can promote the formation of calcium hydrogarnets from the series  $[\text{SiO}_4]\text{Ca}_3 \text{M}^{3+}$ , where  $\text{M} = \text{Al}$  (grossularite) or  $\text{M} = \text{Fe}$  (andradite) by adding alumina or ferrite. The quantity added is typically in the range 20% to 50% (by mass with respect to the mass of Portland cement), i.e., of the same order of magnitude as the amount of silica added. A more particularly preferred composition is constituted by class G Portland cement, 30% to 40% of silica (preferably of the order of 35%) and 20% to 40% of alumina (preferably of the order of 30%).

The mineral phases favoured by these compositions are principally of varying composition, in particular hydrogarnets from the hydrogrossularite series, with a structure derived from calcium garnets  $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$  ( $\text{C}_3\text{AS}_3$ ) with the silica atoms omitted and replacement of the oxygen atoms to which they were bonded by hydroxyl groups. When all of the silicon atoms are replaced,  $\text{C}_3\text{AH}_6$  is obtained. Under the selected experimental conditions (288°C, 20 MPa), those garnets have been shown to be poorly constituted in part, with low reproducibility of crystallisation leading to larger or smaller crystals associated with high heterogeneity in compression test results.

International Patent Application Publication WO01/70646 proposes to develop novel formulations suitable for cementing oil, gas, geothermal wells or the like, based on a Portland and alumina type cement tending to form mineral phases such that the properties of the cement matrix, in particular regarding compressive strength, do not degrade in practice under the effect of a rise in temperature and pressure (250°C-300°C; 20 MPa) and/or chemical attack (brines). The proposed compositions provide a cement matrix included in the Si-Ca-Al

triangle in one of the margarite-haüyne-[epidote/pumpellyite], haüyne-prehnite-[epidote/pumpellyite] and haüyne-prehnite-pectolite composition triangles. In these triangles of the Si-Al-Ca-Na system, many mineral phases exist that are stable under the temperatures and pressures under consideration. The preferred compositions of WO01/7064 are located in the most calcium-rich zones, in particular close to the margarite-[epidote/pumpellyite]-pectolite junctions and margarite-prehnite-pectolite junctions, corresponding to compositions within the Si-Ca-Al triangle approximately in the zone delimited by silicon between 35% and 50%, aluminium between 20% and 38% and calcium between 25% and 35%.

European Patent Number 0 621 247 B describes a cement composition formed from particles having controlled particle size ranges or granulometries. By optimising the packing volume fraction of the particulate materials, cement slurries can be designed that have improved properties while remaining pumpable in normal field conditions.

It is an object of this invention is to provide cement compositions capable of forming a durable matrix at elevated temperatures, especially between 250°C and 400°C, and irrespective of the presence of brines and/or carbon dioxide.

In accordance with the present invention, there is provided a cement composition comprising a mixture of: (i) an hydraulic cement; and (ii) one or more additives that contribute Si, Ca and Al to the mixture; characterized in that it has a mineralogical composition within the Margarite-Quartz-Pectolite region of the Si-Ca-Al phase diagram, and in that the constituents are selected to optimise the formation of Anorthite.

Such compositions are useful for cementing wells such as oil, gas, geothermal, and water wells, in particular such wells that are subjected to high temperatures (in excess of 250°C). Another application for such cements is to serve as an inner lining for pipelines, particularly those that carry brines produced from geothermal wells. The cement lining prevents corrosion of the pipe as the brine is transferred from the wellhead to the power generating station.

Specific modifiers are added to cement powder to promote the formation of Anorthite. At the same time, it is preferred that the density range be as large as possible (1 to 1.94 sg) while maximizing the solid fraction of the slurry to decrease the permeability and increase the compressive strength. It is also preferred that the slurries are stable with respect to sedimentation.

To achieve these goals, the packing between the different components of the blend is optimised by selecting the particle sizes of the cement and additive materials used to make

the slurry. By controlling the particle sizes of the solid constituents of the slurries, the packing volume fraction can be optimised. This technique allows the use of large amounts of solids while making the slurry still easily pumpable and stable with respect to sedimentation.

The Ca-Si-Al ratio of compositions in accordance with the invention is selected to promote the formation of Anorthite. Materials used can be selected in a large variety in term of chemical composition, particle size and morphology.

Firstly, the Si-Ca-Al composition zone can be selected in Si-Ca-Al ternary triangle, using the thermodynamic data existing in geological area.

Then at least three materials containing silicon and/or aluminium of different particle size can be selected. This allows good mixability and a pumpable slurry to be obtained, whatever the slurry density.

The chemical composition can also be selected considering the selected Si-Ca-Al ratio, to optimise total reactivity and fast reactivity of the blend at a given temperature and pressure and the optimised particle size distribution in accordance with the optimised packing volume fraction.

Preferably, the compositions of the invention are located in the Si-Ca-Al triangle, in the zone delimited by silicon between 44% and 57%, aluminium between 18% and 32% and calcium between 18% and 32%.

Compositions in accordance with the present invention can be realised using different materials containing silicon, and/or aluminium which are added to an oilwell cement with or without pozzolanic material. The reactivity and particle size of each material are selected in order to quickly form anorthite and to reach a good mixability respectively.

Microalumina, microsilica and silica/alumina microspheres, metakaolin (calcined kaolinite), kaolinite (clay), fly ash and silica with different particle sizes can be used as silicon and aluminium sources.

The present invention will now be described by way of various examples and in relation to the accompanying drawing which shows the phase diagram of a ternary silicon/aluminium/calcium system showing the blend compositions tested (1 – 9) and various mineral phases.

The composition of the oxides of Portland cement is as given in Table 1 (mass %) and of TXI cement is as given in Table 2:

CaO	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	SO <sub>3</sub>	MgO	Na <sub>2</sub> O	K <sub>2</sub> O
64.2	19.4	5.5	4.5	2.8	2.0	0.1	0.6

**TABLE 1: Oxides composition of a Portland cement**

CaO	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	SO <sub>3</sub>	MgO	Na <sub>2</sub> O	K <sub>2</sub> O
38.5	35.7	5	10.5	Not done	1.8	Not done	Not done

**TABLE 2: Oxides composition of a TXI cement**

The composition containing such cement has to be enriched with silicon and, optionally, aluminium in order to place it into the target elemental regions. However, the composition has to be able to be prepared with a quantity of mixing water such that the density of the slurry is of the order of the densities usually used for cementing an oil well or the like. Furthermore, the slurry must have rheological properties compatible with pumping in such a well.

Eleven slurries with a density between 1.89 g/cm<sup>3</sup> and 1.49 g/cm<sup>3</sup> were thus prepared based on oilwell cement. The formulations are shown in Table 3 below. For the liquid components (fluid loss control agents and antifoaming agent), the quantities are indicated in gallons per sack of Portland cement (1 gps = 3.78 litres per 94 pound cement sack, i.e., 1 gps = 0.070 litres per kilogram of Portland cement). For all of the other components (the solid components) the quantities are given as the percentages by mass with respect to the mass of Portland cement (BMOC = by mass of cement).

All of the proposed formulations were optimised to obtain slurry with a rheology compatible with pumping in a subterranean well, which necessitates adding dispersing agents. Under these conditions, these slurries are stable and pumpable.

Composition #1 is a prior art oil-well cement composition intended for high temperature wells, containing 35% BMOC of silica. The other compositions are compositions of the invention comprising between 0% and 190% BMOC of metakaolin, 0% to 80% BMOC of silica with a grain size close to that of a sand ( $D(v,50) = 330 \mu\text{m}$ ), a Portland cement (average particle size close to  $20 \mu\text{m}$ ), or of micro-silica (average particle size close to  $1.2 \mu\text{m}$ ), and 0% to 72% of fly ash having a diameter between  $50 \mu\text{m}$  and  $400 \mu\text{m}$ .

Further advantageous details and characteristics of the invention will become apparent from the description below of tests established for different examples of additive compositions.

#	1	2	3	3bis	4	5	5bis	6	7	8	9	9bis
Sand	-	-	-	-	40	-	-	-	-	-	-	-
Silica	35	-	-	-	-	-	37	-	-	-	-	-
Micro-silica	-	80	35.5	52	-	37	-	62	31	-	11.5	11.5
Kaolinite	-	-	-	-	-	-	-	-	-	-	-	28
Metakaolin	-	41	40.4	-	74	88.6	88.6	142	143	142	28	-
Microalumina	-	-	-	14	-	-	-	-	-	-	-	-
Fly ash	-	54.6	44.9	44	14.8	55.2	56.4	72	65	53	31.9	31.9
Dispersing agent	0.3	0.3	0.02	0.03	0.06	0.2	0.15	0.25	0.3	0.3	0.15	0.2
Retarder 1	0.3	0.58	0.46	0.44	0.48	0.59	0.59	0.79	0.71	0.61	0.36	0.4
Retarder 2	0.15	0.36	0.29	0.26	0.3	0.37	0.37	0.49	0.44	0.38	0.22	0.25
Fluid loss control agent	0.6	-	1.2	2.5	-	-	-	-	-	-	-	-
Antifoaming agent	0.05	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03

**TABLE 3**

The relative amounts of silicon, aluminium and calcium in these different formulations are as follows:

#	1	2	3/3bis	4	5/5bis	6	7	8	9/9bis
Silicon %	46	57	48	49	50	54	50	44	50
Aluminium %	5	18	20	20	25	28	30	32	25
Calcium %	49	25	32	31	25	18	20	24	25

**TABLE 4**

The following table 5 presents the average particle sizes, which have been used with these slurries. These average particle sizes are not a restrictive factor to form Anorthite and can be higher or lower.



#	D(v,0.5)
Silica	330 $\mu\text{m}$ - 2 $\mu\text{m}$
Kaolinite	10 $\mu\text{m}$ - 2 $\mu\text{m}$
Metakaolin1	2 $\mu\text{m}$
Metakaolin2	10 $\mu\text{m}$
Fly ash	400-50 $\mu\text{m}$

TABLE 5

Table 6 shows the effect of material reactivity, which has to be considered to reach as soon as possible the anorthite matrix.

The cement slurries are prepared, placed in a reactor and heated for 3 days at 150°C and 20 MPa. On the fourth day, the temperature is raised to 300°C over a period of 6 hours to prevent cracking by thermal shock. The cement slurries are kept under these conditions for 28 days. Mineralogical analysis by X ray diffraction is shown in Table 6.

Slurry#3bis contains microalumina and the slurry #3 metakaolin as aluminium and silicon source. These two blends have a Si/Ca/Al ratio that falls well within the phase triangle described above.

Formulation	3	3bis
Metakaolin	-	-
Microalumina	-	-
Quartz	-	-
Xonotlite	*	++
Anorthite	++	++
Wairakite	-	++
Hibonite – 5H	-	-
Riversiderite	+	-

TABLE 6

The following symbols are used in Table 6 and in the other tables below reporting mineralogical analyses:

++: represents a large quantity;

+: represents a small quantity;

\*: trace

-: absence

Formulation #3 containing metakaolin is clearly more reactive, the set cement matrix after one month is mainly composed by anorthite. With formulation #1, wairakite and xonotlite are still well detected after one month and are metastable.

Table 7 shows the effect of Si/Al/Ca blend composition, the material composition and its size on the anorthite formation at short term. The cement slurries are prepared, placed in a reactor and heated for 3 days at 150°C and 20 MPa. On the fourth day, temperature is raised to 300°C over a period of 6 hours to prevent cracking by thermal shock. The cement slurries are kept under these conditions for 5 days. Mineralogical analysis by X ray diffraction is shown in Table 7:

Formulation	1	2	3	4	5	5bis	6	7	8	9	9bis
Metakaolin	-	-	-	-	-	-	-	-	-	-	-
Quartz	+	++	-	-	+	+	++	+	*	+	++
Xonotlite	++	++	+	*	-	-	-	-	-	-	-
Truscottite	-	++	+	-	+	+	-	+	-	+	+
Anorthite	-	++	++	++	++	++	+	++	++	++	+
Diopside	-	-	-	+	-	-	-	-	-	-	-
Wairakite	-	-	-	-	-	-	-	-	-	-	-
Hibonite – 5H	-	-	-	++	-	-	-	-	-	-	-
Riversiderite	-	-	+	-	-	-	-	-	-	-	-

**TABLE 7**

These results show that whatever the Si/Al/Ca blend composition, included in the Si-Ca-Al triangle in one of the Margarite- Quartz - Pectolite composition triangle, anorthite is well formed in the short term. The nearer the blend composition is to the composition of anorthite, the higher the final mineral assemblage contains anorthite, even in the short term.

The material particle size has an effect on the mineral assemblage at equilibrium at 5 days. But anorthite always is found to be the main binder in the short term, showing the high reactivity of the coarser material, at high temperature in the Margarite-Quartz-Pectolite composition triangle.

The material nature is a major factor to form quickly anorthite.

Table 8 shows the effect of final mineral assemblage after 28 days at 300°C on the set cement properties:

Formulation	3	3bis
Compressive strength after 28 days at 300°C psi (MPa)	2570 (18)	2100 (14.5)
Water permeability (mDarcy)	0.02	0.12

TABLE 8

Table 6 shows that metakaolin is more reactive than microalumina: the final mineral assemblage is mainly composed of anorthite. Formulation 3 exhibits after one-month better compressive strength and particularly lower water permeability than formulation 3bis.

This water permeability improvement of “Anorthite” cement is an additional positive factor in term of durability towards brine or carbon dioxide.

## CLAIMS

- 1 A cement composition, comprising a mixture of:
  - (i) an hydraulic cement; and
  - (ii) one or more additives contributing Si, Ca, and Al to the mixture so as to place its mineralogical composition within the Margarite-Quartz-Pectolite region of the Si-Ca-Al phase diagram, and optimise the early formation of Anorthite.
- 2 A cement composition as claimed in claim 1, wherein the additive contributing Al comprises kaolin or metakaolin.
- 3 A cement composition as claimed in claim 1 or 2, wherein the additives include:

kaolin/metakaolin	up to 190% BMOC;
silica	up to 80% BMOC; and
fly ash	up to 72% BMOC.
- 4 A cement composition as claimed in claim 3, wherein the average particle size of kaolin/metakaolin is in the range 2 $\mu$ m to 10 $\mu$ m, of silica is in the range 2 $\mu$ m to 330 $\mu$ m, and of fly ash is in the range 400 $\mu$ m to 50 $\mu$ m.
- 5 A cement composition as claimed in any preceding claim, wherein the mixture has an elemental composition of Si 44% - 57%; Al 18% - 32% and Ca 18% - 32%.
- 6 A cement composition as claimed in any preceding claim, further comprising a liquid added to the mixture to form a slurry.
- 7 A cement composition as claimed in claim 6, wherein the slurry has a density in the range of 1 - 1.94 S.G.
- 8 A method of cementing a well, comprising placing in the well a slurry comprising a mixture of:
  - (i) an hydraulic cement;

- (ii) one or more additives contributing Si, Ca, and Al to the mixture so as to place its mineralogical composition within the Margarite-Quartz-Pectolite region of the Si-Ca-Al phase diagram, and optimise the early formation of Anorthite;  
and
  - (iii) a mix liquid.
- 9 A method as claimed in claim 8, wherein the well has a temperature in the range of 250 – 400°C.
- 10 A method as claimed in claim 8 or 9, comprising forming a lining in a pipe from the slurry.



INVESTOR IN PEOPLE

Application No: GB 0203729.9

Claims searched: 1-10

12

Examiner:

Kathryn Orme

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**Patents Act 1977****Search Report under Section 17****Databases searched:**

UK Patent Office collections, including GB, EP, WO &amp; US patent specifications, in:

UK C1 (Ed.T): C1H

Int C1 (Ed.7): C04B

Other: Online: WPI, EPODOC, PAJ

**Documents considered to be relevant:**

Category	Identity of document and relevant passage	Relevant to claims
X	GB 1525236 (PORTLAND CEMENT MANUFACT) see especially page 2 lines 12-36 and page 3 lines 20-30	1 at least
X	WO 01/70646 A1 (SCHLUMBERGER) see especially page 1 lines 4-9, page 6 lines 13-15, page 7 table 4, sample 7 and page 12 table 10.	1, 5, 6, 7, 8, 9 & 10
A	US 4933031 (BLOMBERG ET AL) see especially column 1 lines 6-13, column 3 lines 25-36 and 64-68, column 4 lines 13-23.	-
X	US 4642137 (HEITZMANN ET AL) see especially column 1 lines 64-68, column 2 lines 1-18, column 4 lines 24-27 and 49-50	1-3 & 5-7
A	US 3486917 (WALLIS) see especially column 3 example 3	-
X	WPI Abstract Accession No. 2000-467906 & JP 2000319052 (Kansai Electric Power Co) 21/11/2000 (see abstract)	1
A	WPI Abstract Accession No. 1996-514784 & JP 8268736 (Chichibu Onada Cement Corp) 15/10/1996 (see abstract)	-

X Document indicating lack of novelty or inventive step

Y Document indicating lack of inventive step if combined with one or more other documents of same category.

&amp; Member of the same patent family

A Document indicating technological background and/or state of the art.

P Document published on or after the declared priority date but before the filing date of this invention.

E Patent document published on or after, but with priority date earlier than, the filing date of this application.